Understanding and Strategies for Controlled Interfacial Phenomena in Lithium-Ion Batteries and Beyond

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Texas A&M University

June 8th, 2017

Project ID #: ES329

Overview

Timeline

- Start date: October 1, 2016
- End date: September 30, 2019
- Percent complete: 17%

Barriers

- Barriers/targets addressed
  - Loss of available capacity
  - Materials evolution during cycling
  - Lifetime of the cell

Budget

- Total funding: $1,333,335
  - DOE share: $1,200,000
  - Contractor share: $133,335
- Funding received
  - FY17: $442,656

Partners

- Interactions/ collaborations
  - J. Seminario (TAMU Co-PI)
  - P. Mukherjee (TAMU Co-PI)
  - Y. Horowitz, UC Berkeley
  - R. Shahbazian Yassar (U. Illinois)
- Project lead: TAMU

Relevance/Objectives

- **Objective:** Evaluate and characterize *interfacial phenomena* in lithiated Si and Li metal anodes and develop strategies leading to *controlled reactivity* at electrode/electrolyte interfaces using advanced modeling techniques based on first-principles.
- **FY 2017 goals**: Characterize SEI formation and cracking of Si nanoparticles; ion transport through SEI blocks; chemo-mechanical degradation; SEI growth rate as a function of electrolyte composition.

- **Addressing targets and barriers**:
    - Anode architectures with better storage capacities; understand and model life-limiting mechanisms incorporating microscopic features.
- **Impact:**
    - Implementation of *stable* Si alloys and Li metal anodes depends on *structural evolution* during battery operation. Understanding SEI reactions, cracking, and dendrite formation will allow rational electrolyte and electrode architecture design.

Relevance/Milestones (17-18)

- Q1/Y1: Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles. (Dec. 16) **Completed**
- Q2/Y1: Identify and quantify Li ion transport mechanisms through SEI blocks (March 17). **Completed.**
- Q3/Y1: Evaluate and quantify the relative influence of mechanical and chemical degradation interplay in Si active particles. (June 17) **In progress**
- Q4/Y1: Characterize SEI growth as a function of SEI composition. Compare the SEI rate growth with experimental trends in the literature and from collaborators (Go-No Go); if there is any disagreement revise respective modeling approach. (Sept.17)
- Q1/Y2: Complete analysis of effects of Li-substrate interactions on Li deposition. (Dec.17)
- Q2/Y2: Complete study of SEI reactions over Li deposits. (March 18)
- Q3/Y2: Complete analysis of operating conditions on dendrite growth. (June18)
- Q4/Y2: Complete evaluation of co-deposition effects. Establish comparisons with experimental trends (Go-No Go) (Sept. 18)

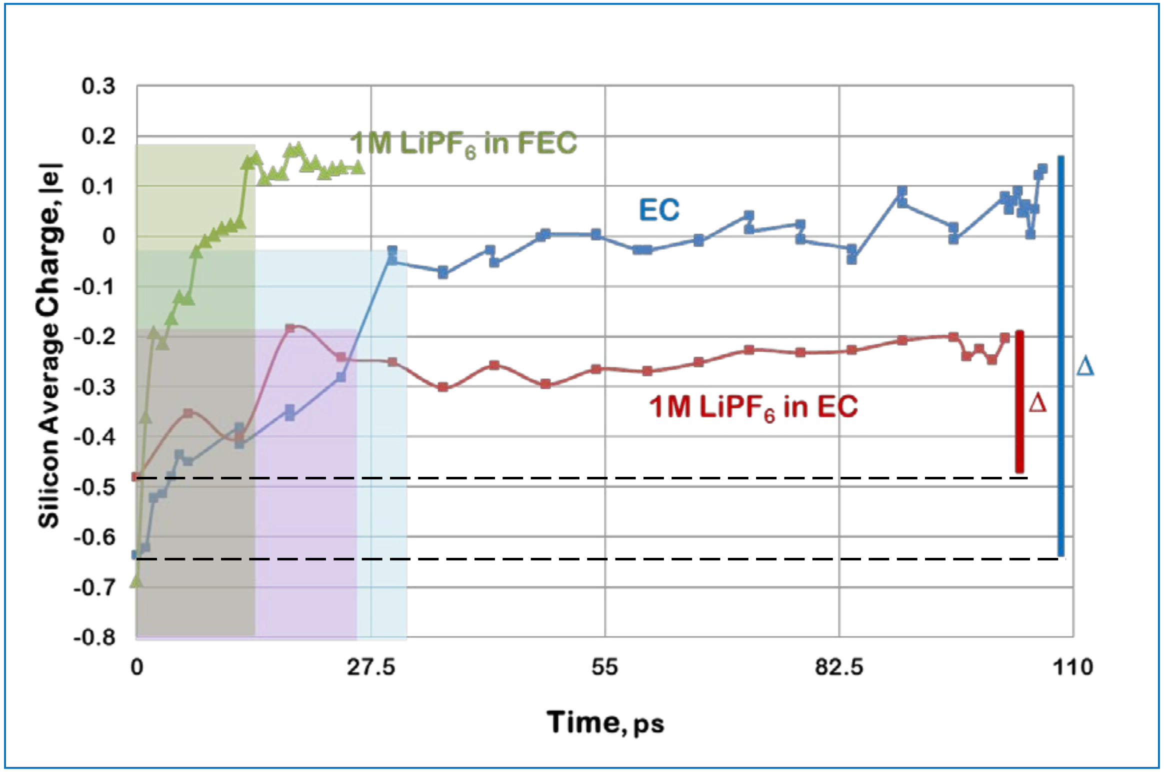
Approach/Strategy

- **Overall technical Approach**:
  - Interfacial problems (SEI growth, Si particle cracking due to volume expansion, Li dendrites formation) addressed with *synergistic multiscale modeling* (ab initio, classical molecular dynamics, and mesoscopic level).
  - All findings rigorously compared with experimental evidence. In many cases, first-principles approach allows prediction and interpretation of new and experimentally observed phenomena.
  - Addresses technical barriers/targets: Rate of SEI growth as a function of electrolyte composition characterizes *SEI evolution*. Cracking of Si nanoparticles, identification of SEI reforming, and dendrites formation elucidate *anode capacity loss* and *cell lifetime*.
  - Collaboration within TAMU and with experimental groups (UC Berkeley and UI Chicago).
- **Progress towards FY17 and FY18 milestones and Go/No Go decisions**: Rate of growth of SEI products demonstrated. Modes of cracking of Si particles elucidated; on-going self-healing and protective films study. Ion transport mechanisms through SEI characterized. Microscopic origin of dendrite formation analyzed.

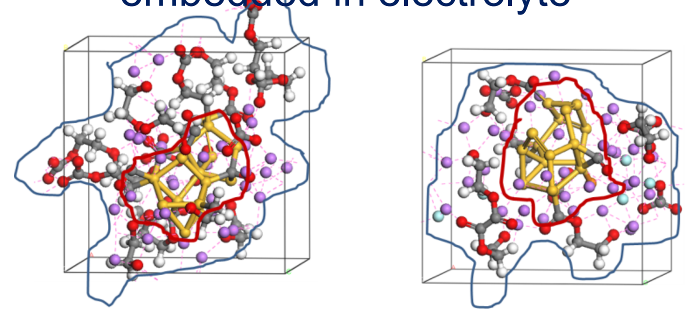
Technical Accomplishments: Barriers Addressed

- **Loss of available capacity**
  - ***Identified SEI growth*** allows evaluation of Li irreversible retention capacity of the film.
- **Materials evolution during cycling**
  - Study reveals ***cracking of SEI film*** as the particle lithiates during cycling for small 4nm and larger 0.5 μm particles.
- **Lifetime of the cell**
  - ***Characterized cracking and dendrite formation*** during lithiation provide insights for development of protection strategies for extended cell lifetime.

Technical Accomplishments: SEI growth as a function of electrolyte composition

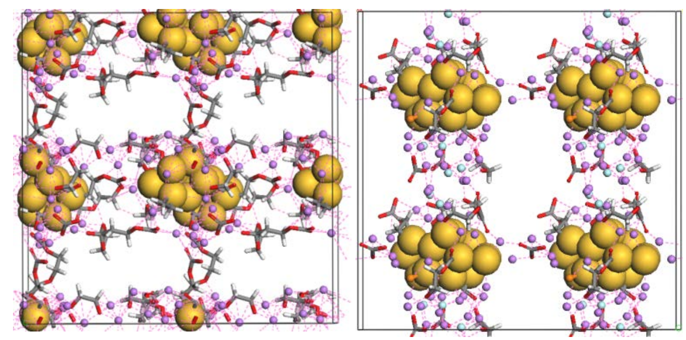


lithiation of Si nanoparticle embedded in electrolyte



without salt
thicker
SEI has only organic components

with salt
thinner SEI contains LiF and organic components

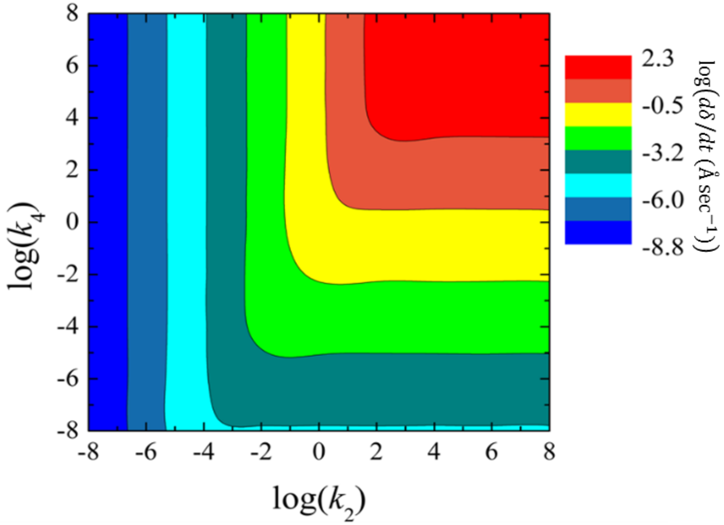


Nanoparticle network through continuously growing SEI

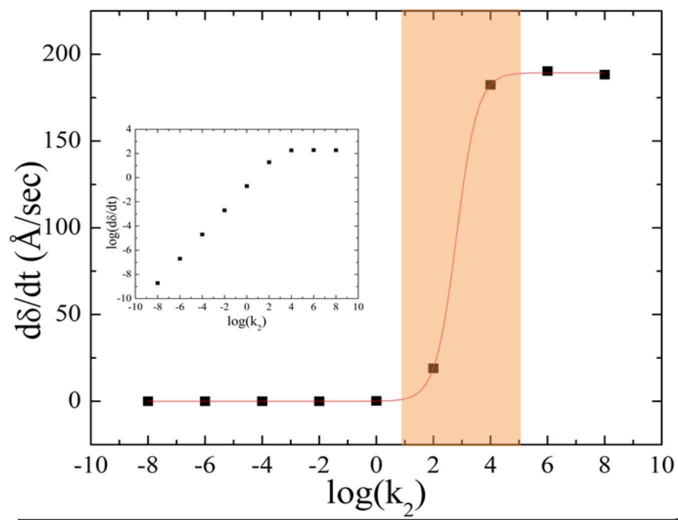
rate of growth significantly dependent on electrolyte composition

Milestone Q1/Y1 : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles.

Technical Accomplishments: SEI growth as a function of electrolyte composition



Effect of EC reduction rate (k_2) and Li_2EDC formation rate (k_4) on SEI thickness growth rate. The thickness growth rate is controlled by the EC reduction step (k_2).[a]



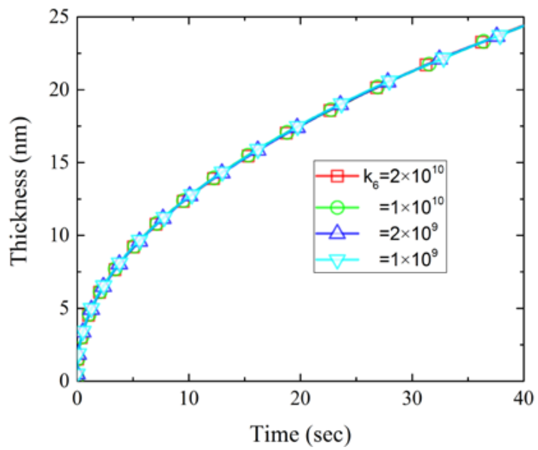
SEI growth rate ($\frac{d\delta}{dt}$) significantly depends on reduction rate:

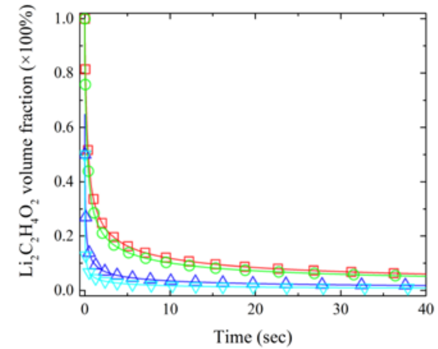
1. SEI grows slowly when $k_2 < 1$sec^{-1} and it grows very fast when $k_2 > 10^4$ sec^{-1}.
2. There is a transition region ($1 < k_2 < 10^4$) between low growth rate and high growth rate.

[a]*Journal of Electrochemical Energy Conversion and Storage*, **13**, 031002 (2016).

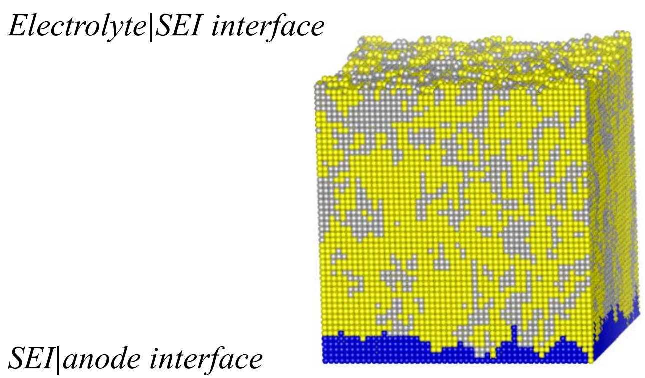
Milestone Q1/Y1 : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles.

Technical Accomplishments: SEI growth as a function of electrolyte composition





Effect of EC^-(open) reduction rate (k_6) on the evolution $Li_2C_2H_4O_2$ volume fraction in the SEI film. The formation of $Li_2C_2H_4O_2$ only happens at the initial stage of SEI formation.



Component distribution in the SEI film.
$Li_2C_2H_4O_2$ only forms at SEI|anode interface.

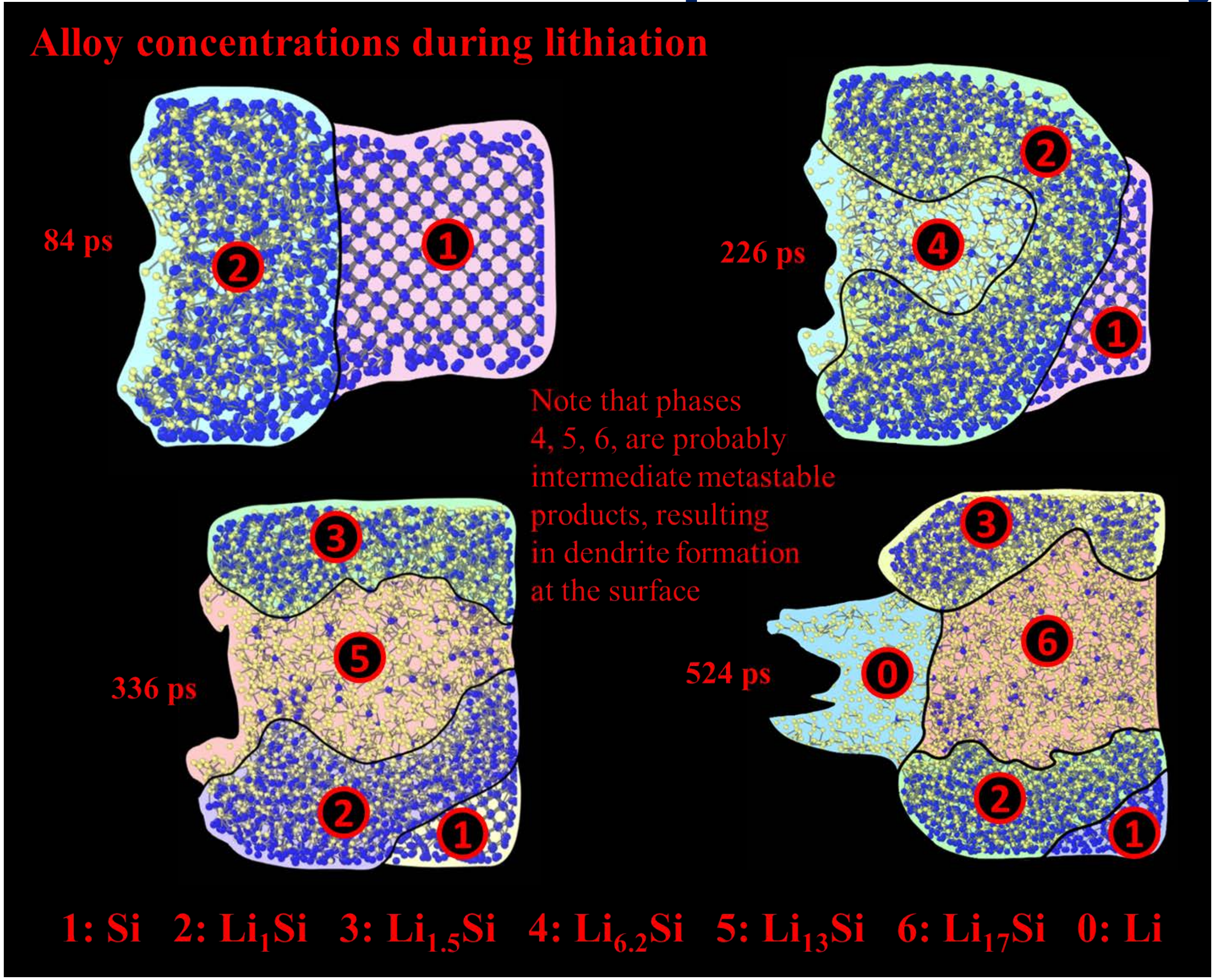
Chemical and electrochemical reactions in the model

EC+*→EC*,	EC adsorption k_1
EC*+e$^-$ → EC^-(closed),	EC reduction k_2
EC^-(closed) →EC^-(open),	Structure transformation k_3
EC^-(open)+Li^+ →Li_2EDC,	Li_2EDC formation k_4
EC^-(open)+Li^+ →Li_2BDC,	Li_2BDC formation k_5
EC^-(open)+e$^-$ →$C_2H_4O_2^{2-}$,	EC^- reduction to $C_2H_4O_2^{2-}$ k_6
$C_2H_4O_2^{2-}$+2Li^+ →$Li_2C_2H_4O_2$,	$Li_2C_2H_4O_2$ formation k_7

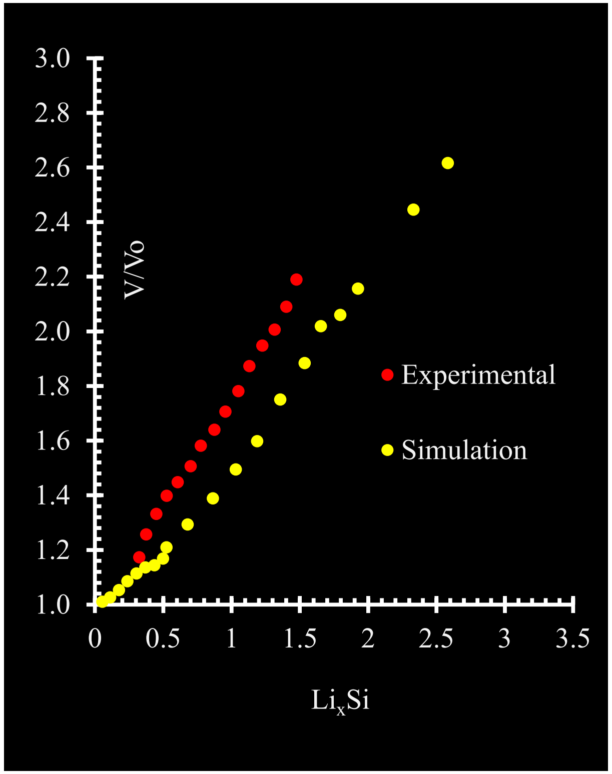
Milestone Q1/Y1 : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles.

Technical Accomplishments:

Lithiation and expansion of crystalline silicon



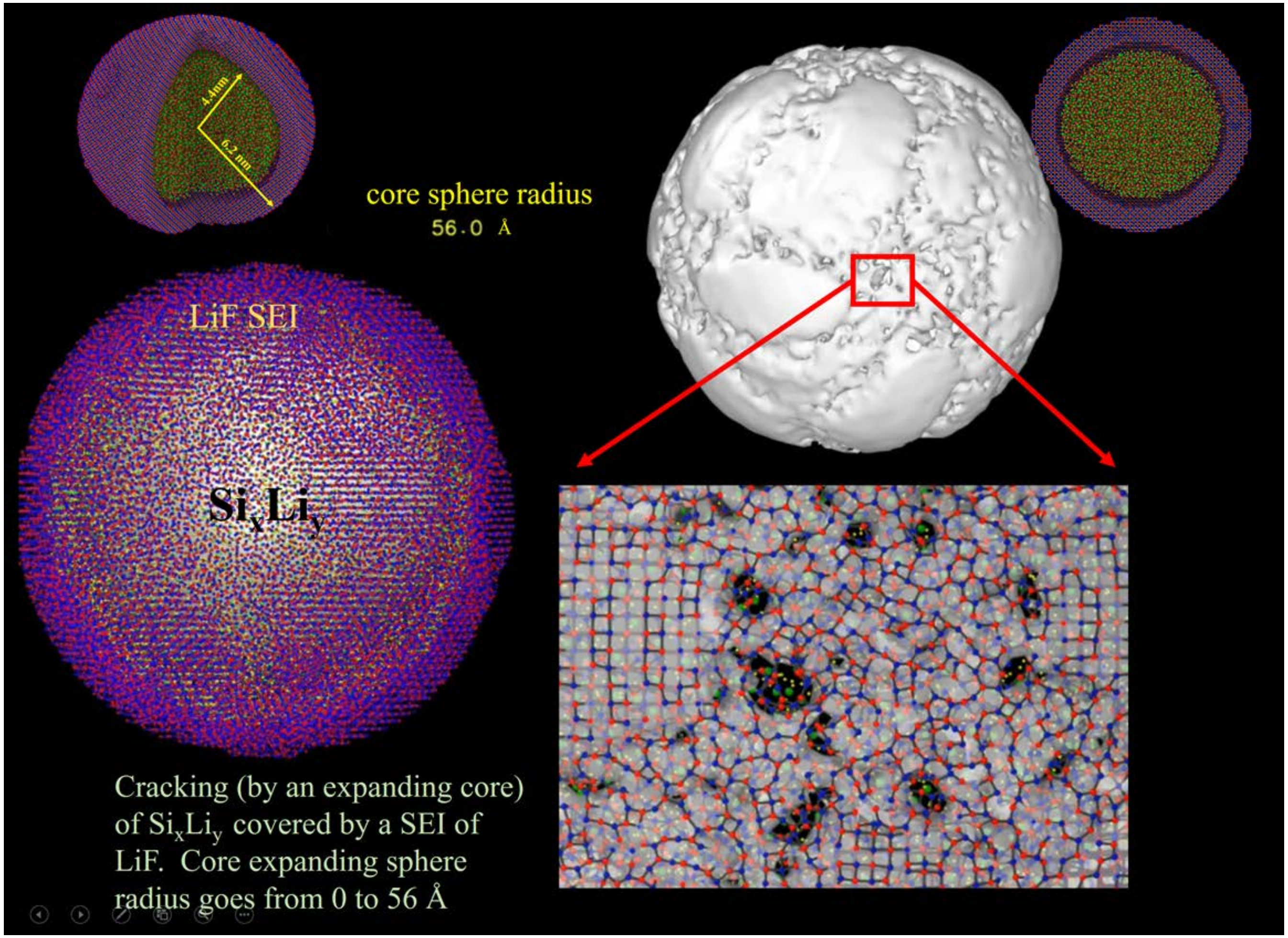
alloying and amorphization takes place by regions



Exp: Jerliu et al JPCC, 118, 9395, (2014)

Milestone Q1/Y1: : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles

Technical Accomplishments:
Cracking of a 4.4 nm Li_xSi_y nanoparticle



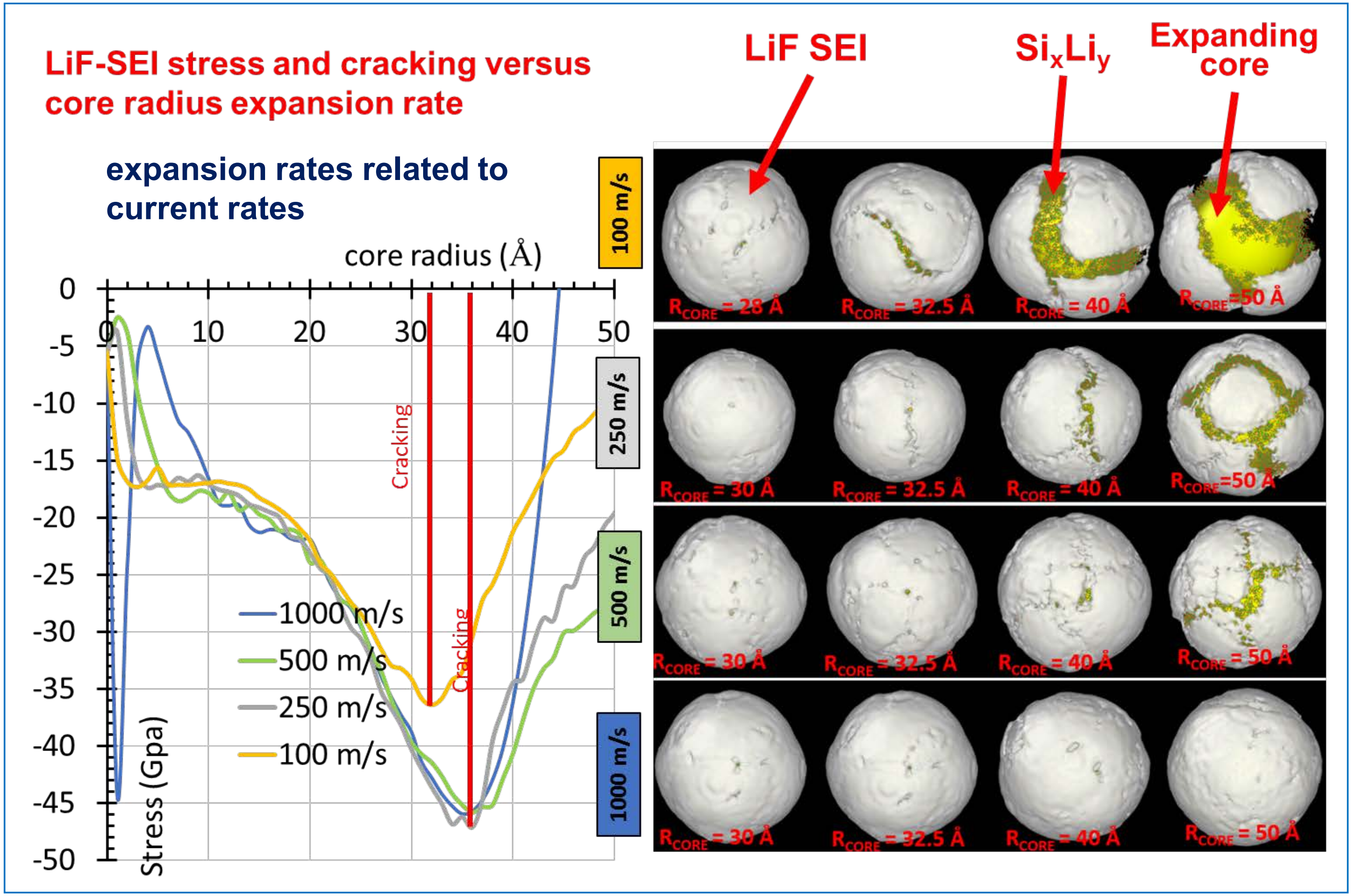
Si nanoparticle of 4.4 nm covered by a LiF film of 1.8 nm

Molecular dynamics simulations allow observation of stress-induced cracking due to expansion of the Li_xSi_y alloy core.

Note formation of holes due to bond breaking and posterior cracking

Milestone Q1/Y1 : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles. ✓

Technical Accomplishments:
Cracking of a 4.4 nm Si nanoparticle

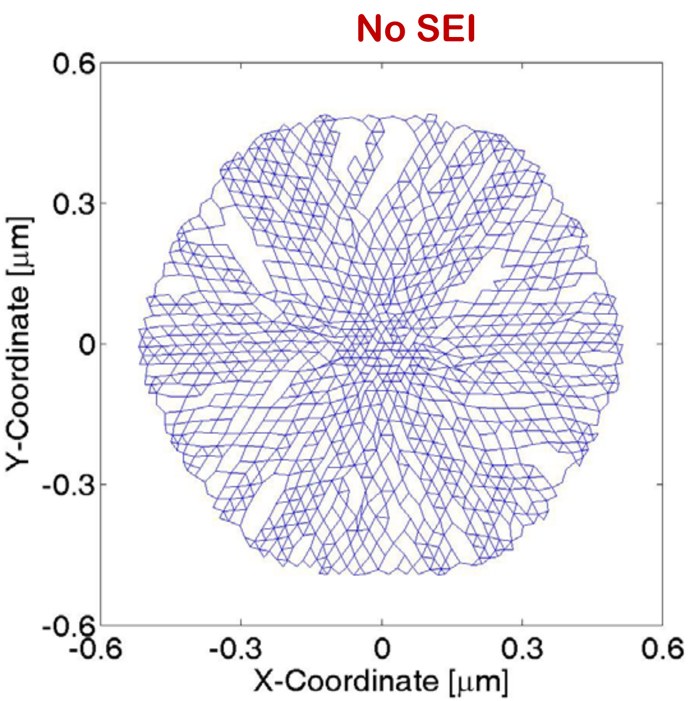


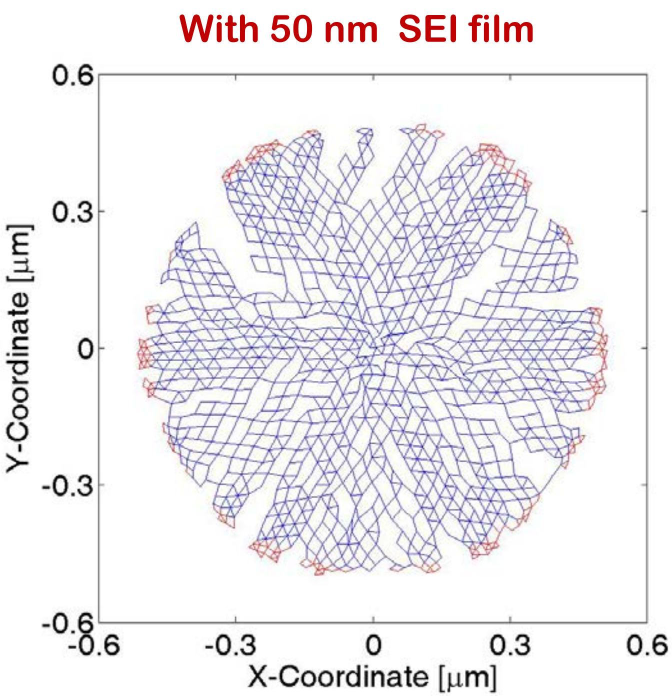
Milestone Q1/Y1 : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles. ✓

Technical Accomplishments:

Damage Evolution: Crystalline 500 nm Si particle

Damage profile for one lithiation/delithiation cycle at 1C





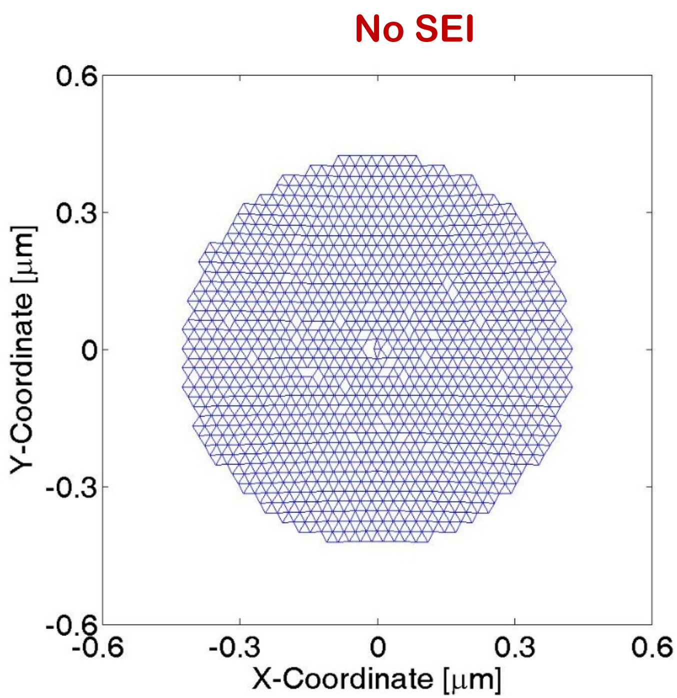
Large strain inhomogeneity between Li rich and Li poor phase exacerbates fracture

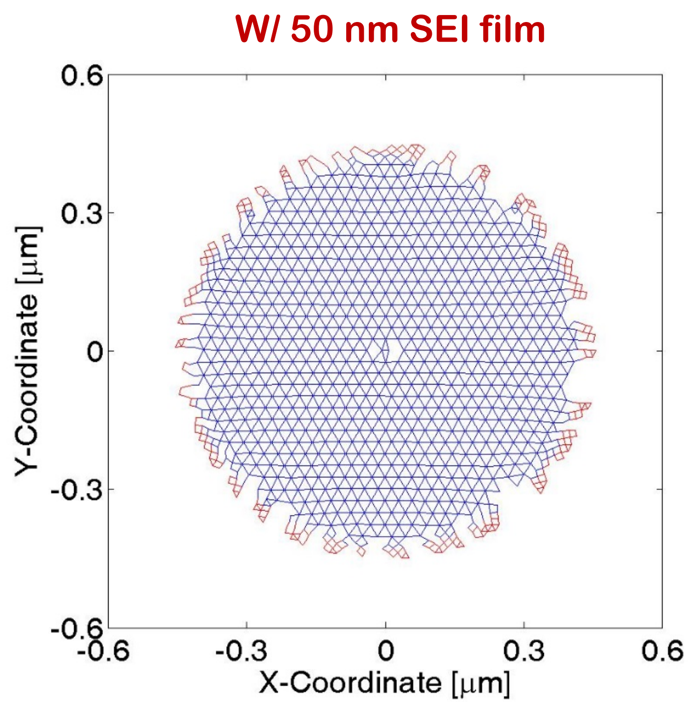
Milestone Q1/Y1 : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles.

Technical Accomplishments:

Damage Evolution: Amorphous 500 nm Si particle

Damage profile for one lithiation/delithiation cycle at 1C





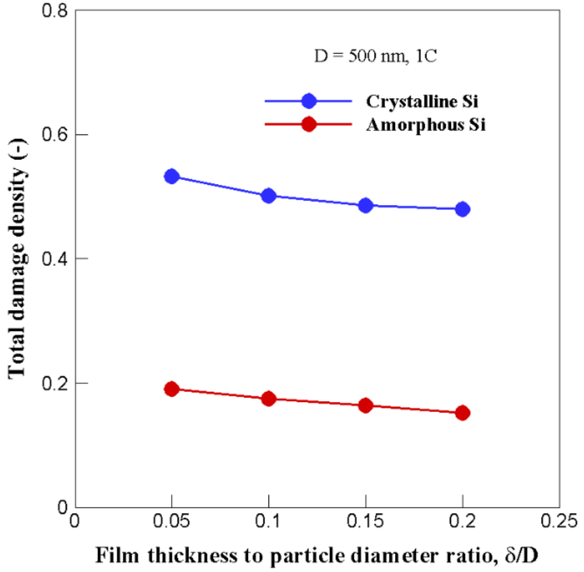
Volumetric strain more homogeneously distributed throughout single phase amorphous Si particle → lower damage compared to two-phase Si

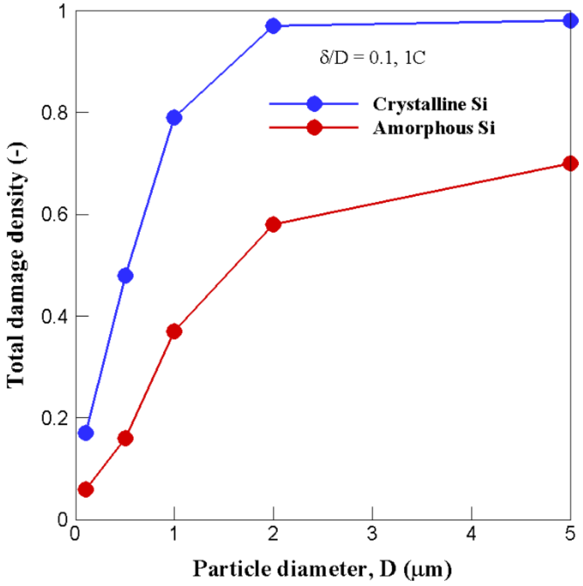
Milestone Q1/Y1 : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles.

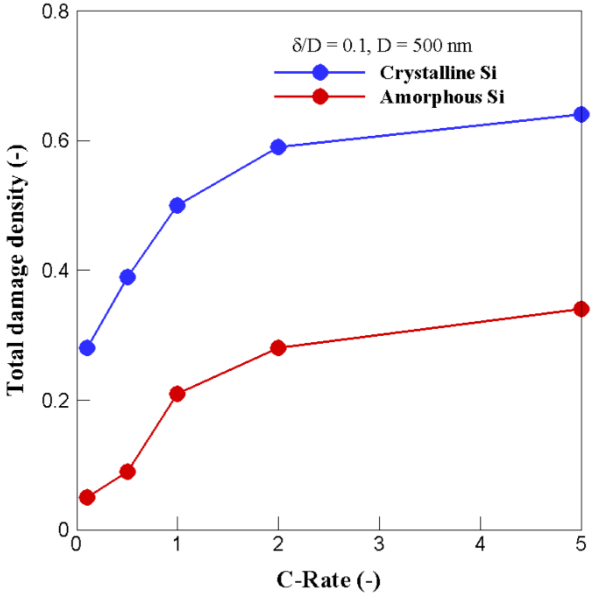
Technical Accomplishments:

Damage Density Evolution

$$\text{Damage Density} = \frac{\text{No.of broken bonds}}{\text{Total no.of bonds in Silicon+SEI Film}}$$



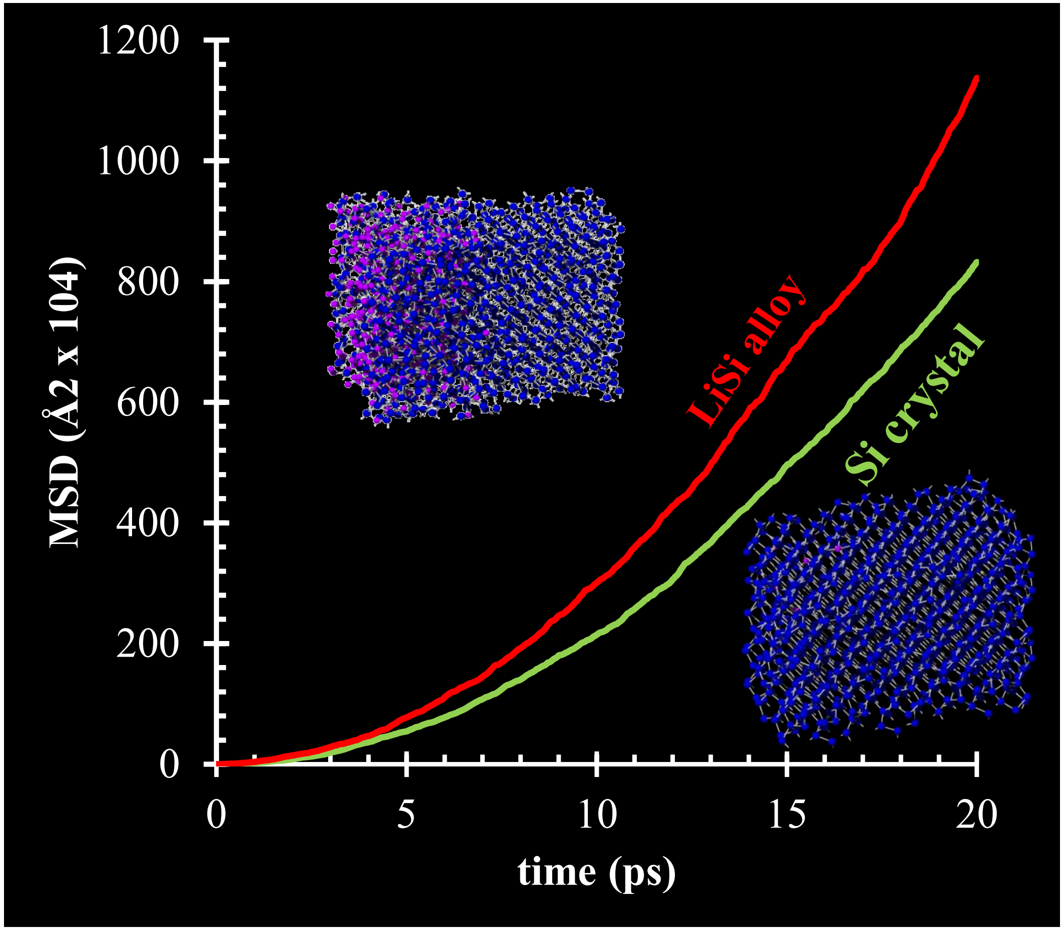




Milestone Q1/Y1 : Characterize SEI nucleation and modes of cracking as functions of SEI composition on lithiated Si nanoparticles. ✓

Technical Accomplishments:

Ionic transport through lithiated phases



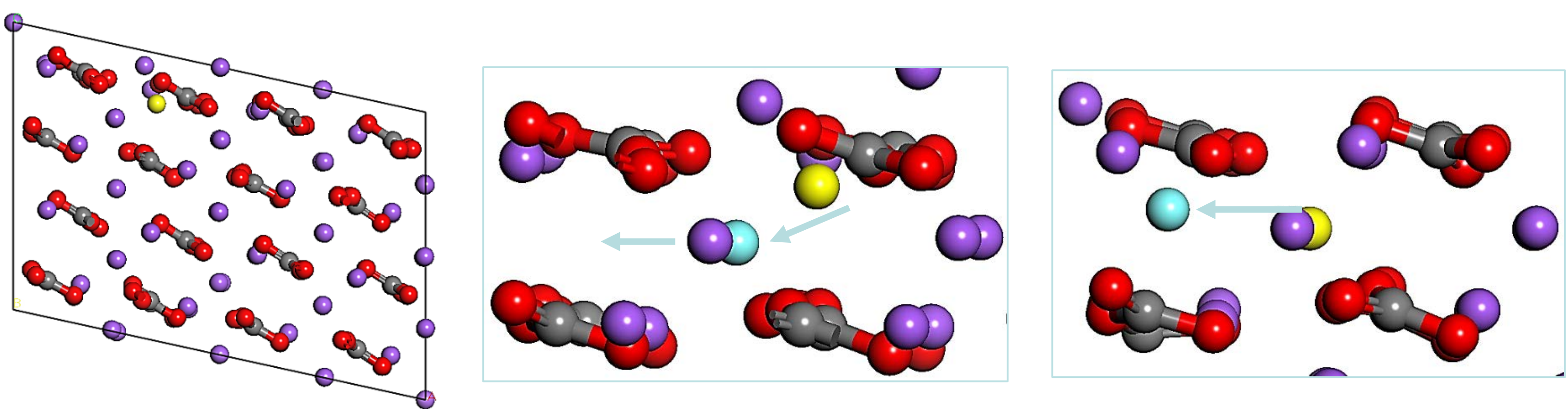
Slope of mean square displacement is proportional to the diffusion coefficient of Li ions through the amorphous alloy (red), compared to Li through the crystalline Si phase

Milestone Q2/Y1: Identify and quantify Li ion transport mechanisms through SEI blocks

Technical Accomplishments:
Ionic transport through SEI blocks

Na^+ diffusion studied through 2 SEI layer blocks

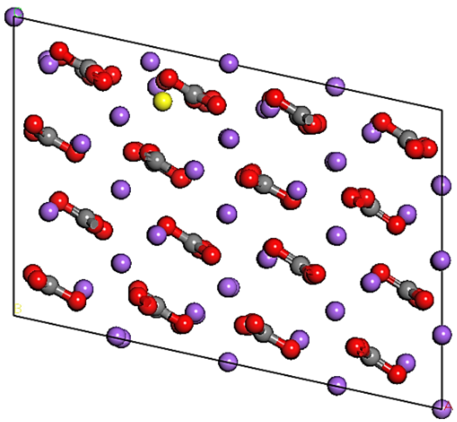
Models	Diffusion Mechanisms	E_m (eV)	E_a (eV)	a^2 (cm^2)	$D(cm^2.s^{-1})$	
					300K	1000K
Na_2CO_3	Knock-Off	0.84	1.04	6.50E-16	5.09E-35	6.54E-13
Na_2O	Direct-Hopping	0.10	2.62	3.52E-15	7.61E-47	4.91E-16



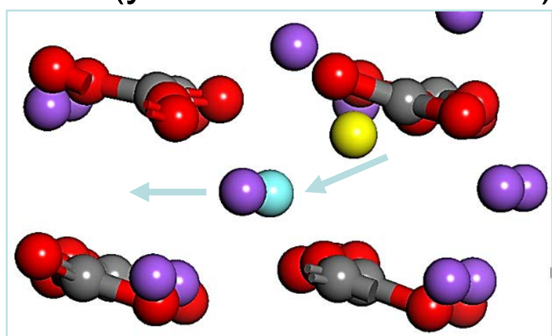
Milestone Q2/Y1: Identify and quantify Li ion transport mechanisms through SEI blocks

Technical Accomplishments:
Ionic transport through SEI blocks

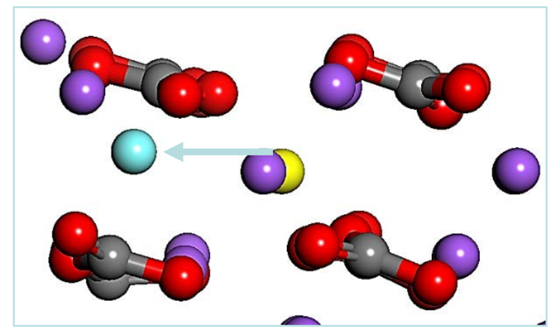
Na^+ diffusion through Na_2CO_3; knock-off mechanism



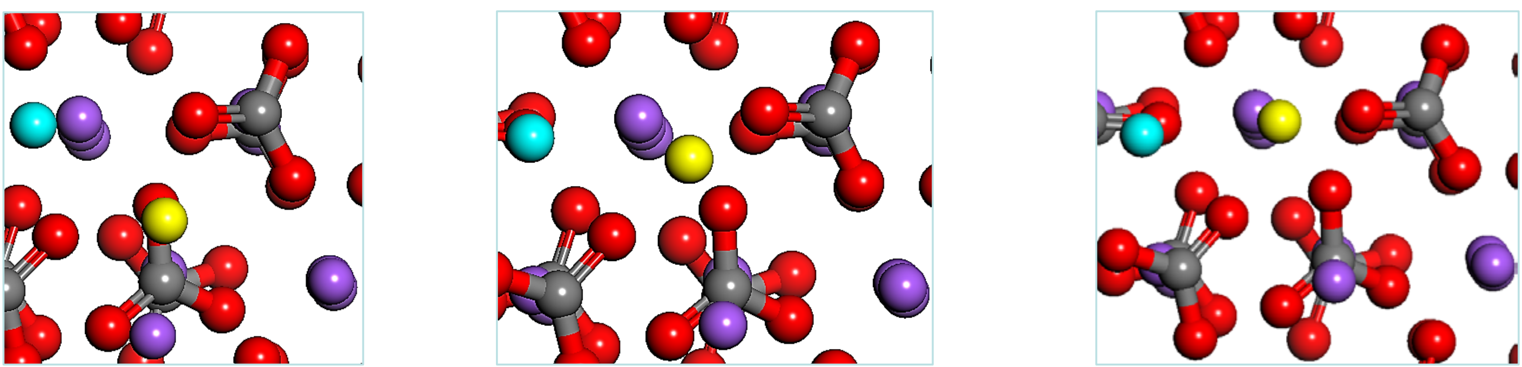
Initial (yellow knocks off blue)



final



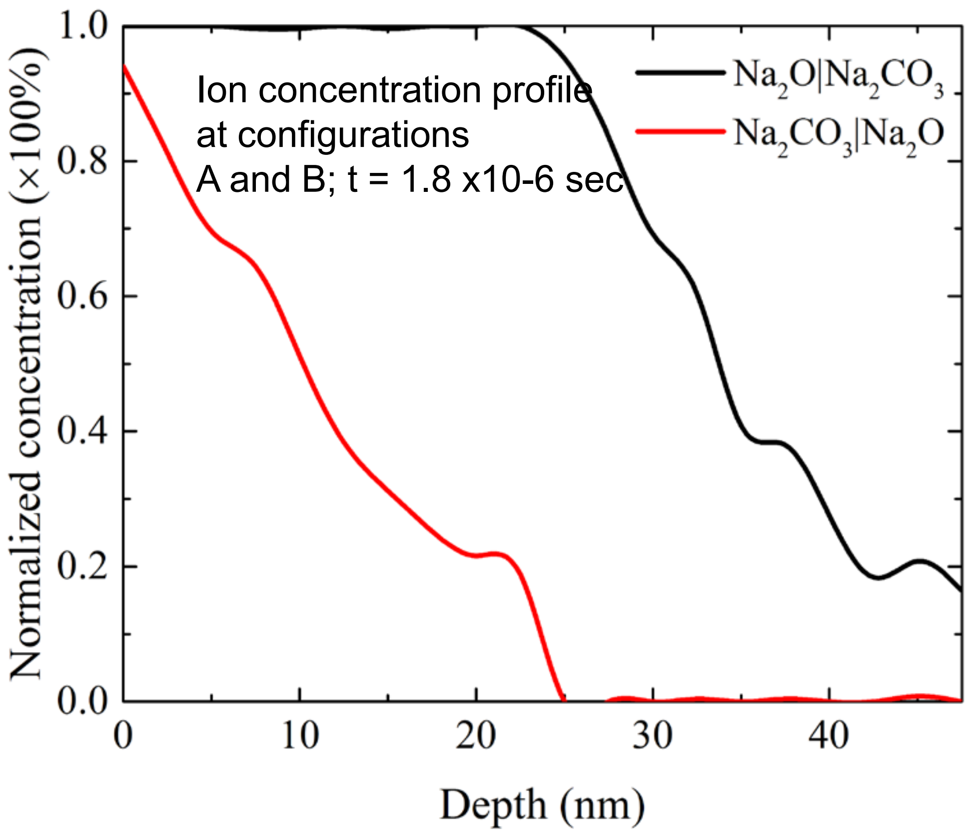
Intermediate images; top view

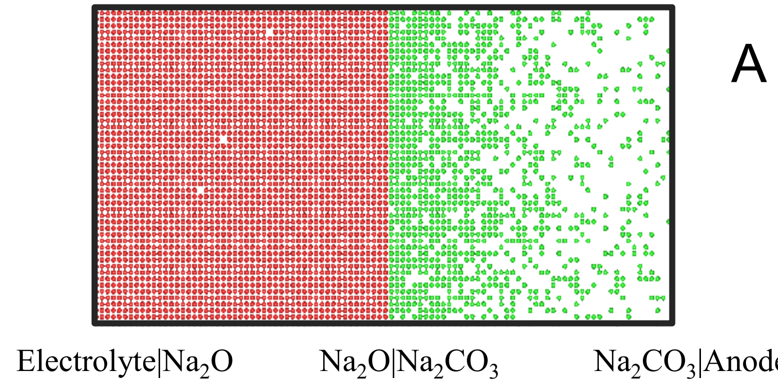


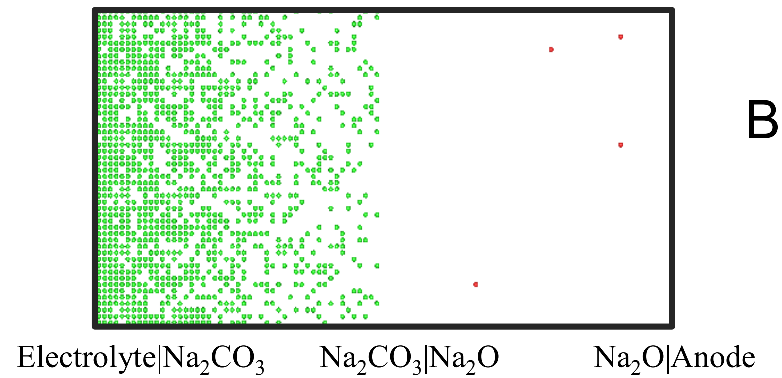
Milestone Q2/Y1: Identify and quantify Li ion transport mechanisms through SEI blocks

Technical Accomplishments:

Effect of SEI nucleation mode on ionic transport





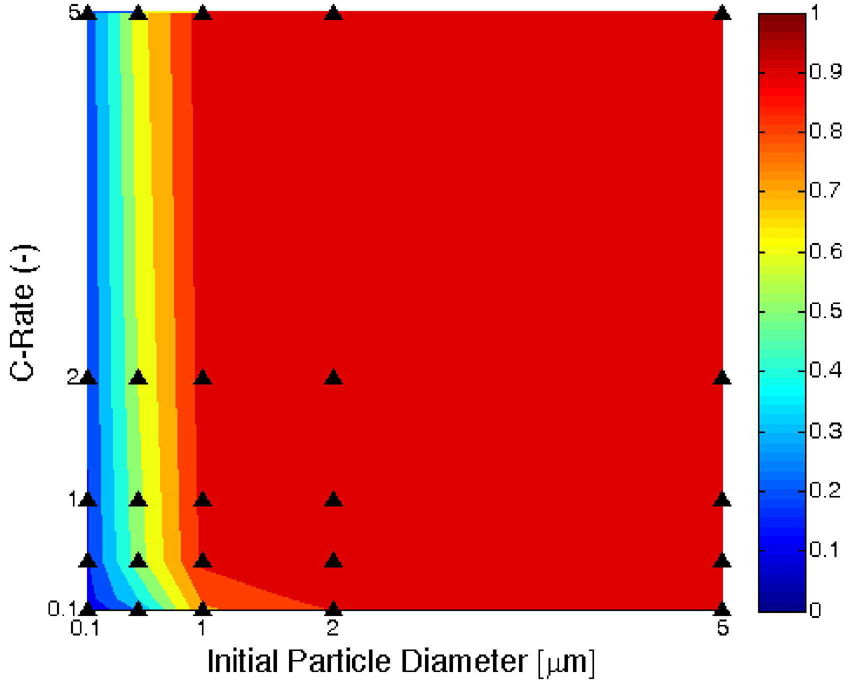


Assembly of the blocks (see A&B) with respect to anode & electrolyte influences ionic transport and location of bottlenecks

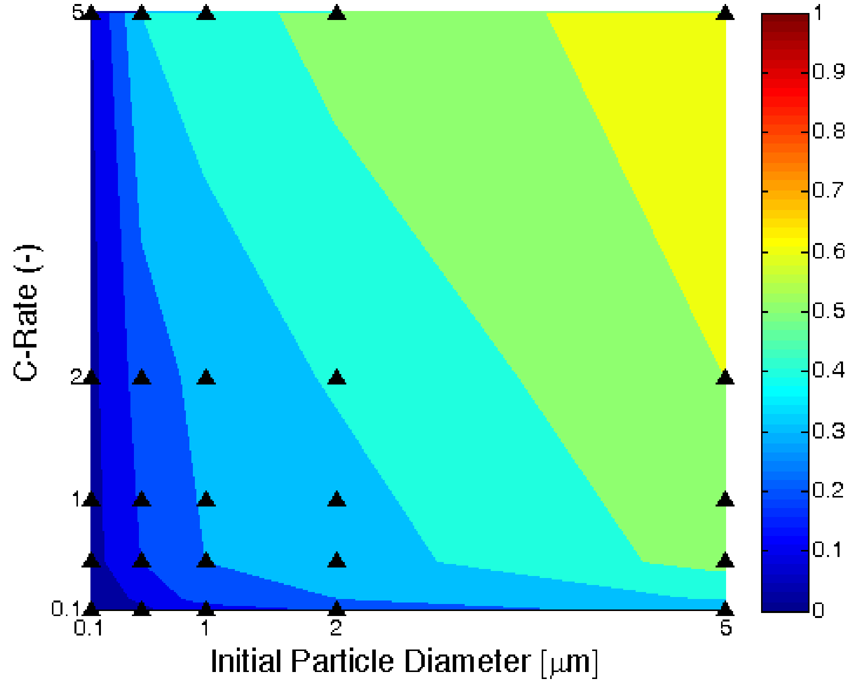
Interstitial Na^+ distribution (red and green dots mean Na ion concentration)

Milestone Q2/Y1: Identify and quantify Li ion transport mechanisms through SEI blocks

Technical Accomplishments: Mechano-Electrochemical Interaction Phase Map



Crystalline Si with film



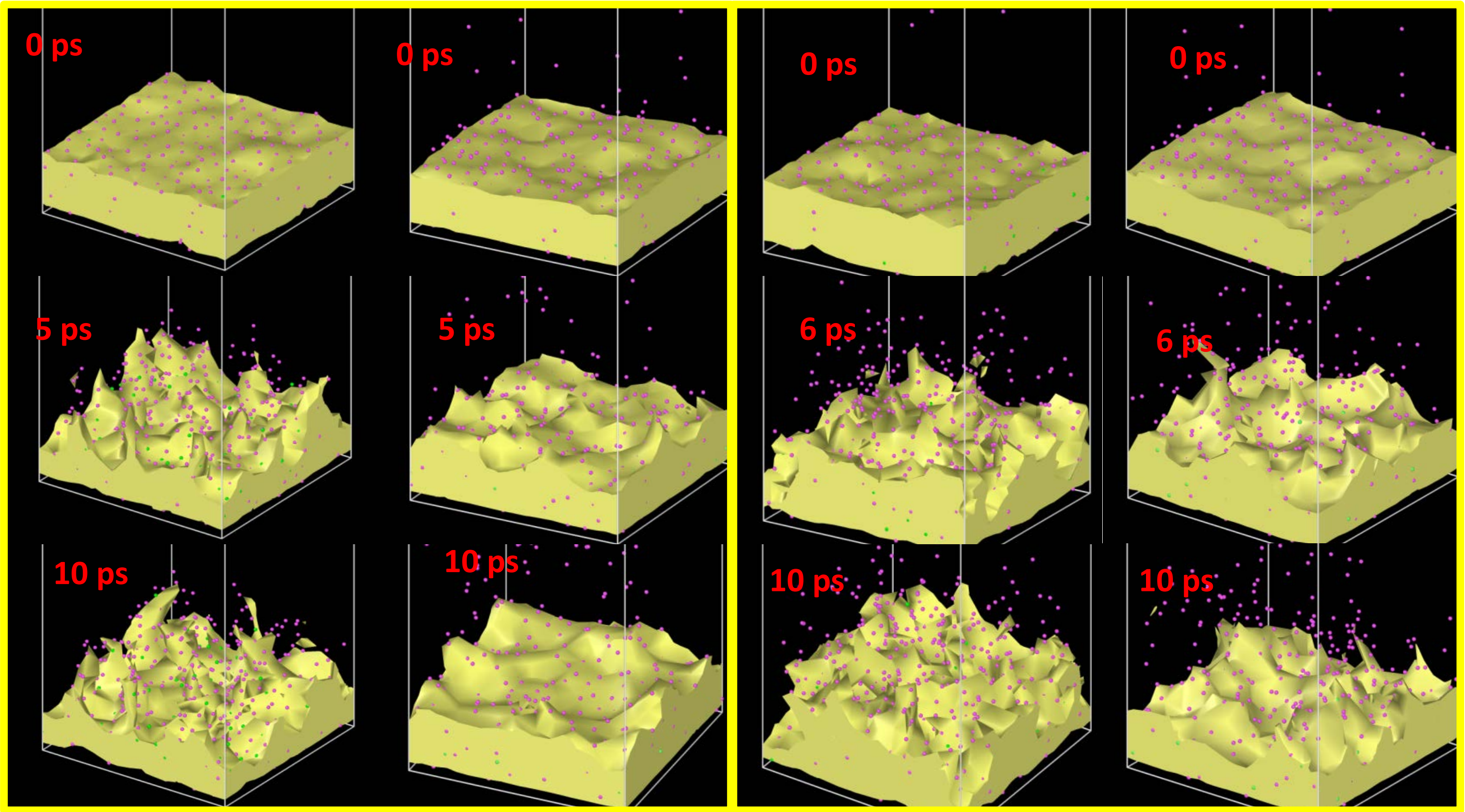
Amorphous Si with film

Crystalline Si shows greater propensity for fracture compared to amorphous Si.
Si particle diameter ~ 200-300 nm is preferred to reduce the magnitude of fracture.

Milestone Q3/Y1: Evaluate and quantify the relative influence of mechanical and chemical degradation interplay in Si active particles.

Technical Accomplishments: Deposition of Li on Li_xSi_y substrates

Under constant charge **Under a charge gradient**



Dendrites formed at the surface of the Li_xSi_y electrode. Different electrolytes used at left and right panels of each case.

Milestone Q1/Y2: : Complete analysis of effects of Li-substrate interactions on Li deposition

Responses to Previous Years Reviewers' Comments

New project,
it was not reviewed last year

Collaboration and Coordination with Other Institutions

- Texas A&M University (prime): Prof. Jorge Seminario (Co-PI), classical MD simulations, and Prof. Partha Mukherjee (Co-PI) , mesoscopic modeling, have contributed large part of the reported work.

- UC Berkeley: Sum frequency generation vibrational spectroscopy (Y. Horowitz, Hui-Ling Han, Gabor Somorjai, UCB) is used together with ab initio molecular dynamics simulations (TAMU) to characterize SEI formation at the surface of amorphous Si anodes.

- University of Illinois at Chicago: Graphene oxide and other coating materials are examined as protection of Cu current collectors where Li is plated. The surface changes and reactions are characterized by surface science techniques (Prof. Shahbazian-Yassar, UIC), and DFT and AIMD simulations (TAMU)

Remaining Challenges and Barriers

- We have made significant progress determining a) how the SEI layer nucleates on Si nanoparticles, and b) how particles of various sizes are lithiated, expand, and crack. We still need to determine the ***effects of specific protective (self-healing) coatings on such cracking***.
- We reported ***ionic conductivity*** through individual and sequential SEI blocks. Additional challenges due to ***more complex layers, SEI cracking, and restructuring*** will be addressed.
- Preliminary analyses have been reported regarding dendrite formation, additional work needs to address the ***effects of salt concentration, substrate roughness, and current rate on Li plating***.

Proposed Future Work

- **Rest of FY17**:
  - influence of mechanical and chemical degradation interplay in Si active particles
  - SEI growth as a function of electrolyte composition

- **FY18:**
  - effects of substrate topography and chemistry on Li deposition
  - SEI reactions over Li deposits
  - effects of operation conditions on dendrite growth
  - effects of co-deposition on Li plating

Any proposed future work is subject to change based on funding levels

Summary Slide

- **Relevance:** **Elucidation of SEI formation and cracking on Si alloys and dendrite formation on Li metal is crucial for *controlling irreversible capacity loss* and *improving lifetimes*.**
- **Approach:** **Characterization of issues that impede extended lifetimes in Si and Li metal anodes through *multiscale modeling*: from electronic structure and dynamics, through atomistic classical molecular dynamics, and mesoscopic modeling.**
- **Technical Accomplishments:** **characterization of SEI formed in Si nanoparticles under different electrolytes; lithiation and cracking of Si nanoparticles of 4nm and 500 nm; ionic diffusion through SEI blocks; analysis of dendrite formation.**
- **Collaborations:** **Synergistic multiscale modeling approach (TAMU); SEI formation in amorphous Si surfaces (with UCB); effect of current collector coatings on dendrite formation (with UIC).**
- **Future Work:** **Protective self-healing coatings for Si anodes and further understanding of deposition effects on Li metal.**